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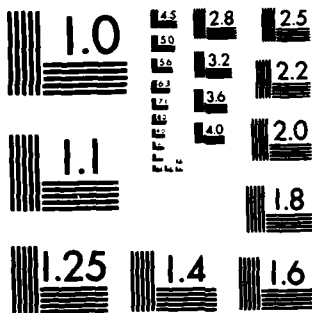
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A STEREOSPECIFIC VAPOR DETECTOR

FINAL REPORT

By

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March 27, 1984

U. S. ARMY RESEARCH OFFICE

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18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) host-guest materials, specific sensors		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) It has been discovered that it is possible to produce stable intimate mixtures of normally incompatible materials (such as sodium chloride and benzene) by vapor co-deposition on a very cold surface. Some spectroscopic and chemical properties of the novel materials have been investigated, and it is concluded that they show potential for the development of specific sensors.		

BRIEF OUTLINE OF RESEARCH FINDINGS

The aim of this project was to find out whether molecular shape specific footprints could be produced on the surface of suitable matrices by vacuum vapor co-deposition of template molecules and of the matrix host material onto a very cold substrate. Should this turn out to be possible, ways to detect specific adsorption of guest molecules on such modified surfaces were to be explored next. The matrix material was to be chosen so as to be stable at room temperature.

The following host materials were tested: NaCl, KBr, CsI, CsF, CuCl, As₂S₃, As₂O₃, Te.

The guest materials numbered several dozen and represented a broad spectrum of polar and nonpolar organic molecules.

The work proceeded in several steps:

(i) The first question has been answered in the affirmative: It is possible to incorporate organic molecules inside inorganic matrix materials in a highly non-equilibrium but kinetically stable situation. Whether a molecule is permanently incorporated depends above all on its polarity and tendency to aggregate, on the properties of the host matrix material such as its heat of vaporization, and on the temperature and rate of deposition.

The ease with which the volatile organic guest molecules can be removed not only from the surface but also the body of the matrix by heating the composite powder under reduced pressure depends strongly on the nature of the matrix host. Removal of naphthalene from CuCl takes hours at 100°C, its removal from CsI is undetectable after hours at 450°C. At room temperature, carbon dioxide escapes from NaCl powder after a few days at room temperature, but it stays for weeks in NaCl which has been compacted into a pellet under pressure.

An example of the results obtained is provided in Table 1, which lists the results for seventeen organic molecules as guests in NaCl and CsI hosts. The deposition temperature was 77K and the test for entrapment was heating the composite sample to 100°C for one hour under high vacuum. If the sample remain incorporated, as judged by IR spectroscopy, the result is listed as positive, otherwise as negative.

Table 1

Incorporation of Guest Component
Inside of the Crystal Lattice

No.	Guest Component	NaCl	CsI
1	benzene	+	+
2	toluene	+	+
3	naphthalene	+	+
4	anthracene	+	+
5	diphenylmethane	+	+

6	dodecamethyl-	+	+
	cyclohexasilane		
7	chlorobenzene	-	+
8	p-dichlorobenzene	+	+
9	pyrrole	-	-
10	acetophenone	-	+
11	anisole	-	+
12	phenol	-	-
13	p-fluorophenol	-	+
14	2,6-dichlorophenol	+	+
15	1-adamantanol	+	+
16	1-adamantanethanol	+	+
17	1-adamantyl azide	+	+

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We believe that these observations have obvious technological implications, for instance for the storage of sensitive or noxious substances. A patent application has been filed.

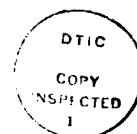
(ii) The next question had to do with the state of aggregation of the guest molecules: if these molecules are not dispersed individually, any footprints which they might leave on the host surface upon evaporation may have inappropriate shapes for the desired purpose.

We have used two approaches to the determination of the state of aggregation of the guest. These were first, spectroscopy, and second, photochemistry.

Fluorescence, uv-visible absorption, ir absorption, and ^1H and ^{13}C nmr measurements were performed on a variety of samples. The results for matrices deposited at 77K were mostly indicative of a moderate to considerable degree of aggregation.

The following photochemical tests were performed:

(a) Anthracene was deposited in NaCl, KBr, CsI, and CuCl at various temperatures. Thermal stability of the anthracene-CsI composite material was tested for several hours at 400° and 10^{-5} torr. No escape of anthracene was observed even after several hours. The depositions were performed at 10K as well as 77K and photochemical dimerization of anthracene was investigated for these mixed materials as well as a reference material, which was represented by crystals of anthracene simply ground with the host material and pressed into a pellet. The irradiation was performed under several sets of conditions: 77K, -4°C, room temperature, and 100°C. The wavelength of the light used was found to have no effect on the results, which are summarized below (+ means dimerization is detectable, - means it is not, in the time stated).



irradiation temp.	CuCl deposited at		CsI deposited at			NaCl deposited at		KBr deposited at
	9K	mix	9K	77K	mix	77K	mix	77K
77K			- 5 hours		- 7 hours			
-4°C			- 19 hours	+ very little after 24 hrs.	+ 6 hours	- 14 hours	+ 6 hours	- 14 hours
ROOM	- 17 hours	+ 5 hours	- 27 hours	+ 13 1/2 hours	+ 3 1/2 hours	- 14 hours	+ 5 1/2 hours	+ 5 1/2 hours
100°C	Complete diffusion out of the matrix after a few hours		- 9 hours	+ 5 hours		+ 10 hours		

While the reference sample which contains anthracene microcrystals dimerizes readily under essentially any conditions except for the lowest temperatures, it is apparent that our composite materials behave quite differently. In particular, anthracene deposited in cesium iodide at 9K does not dimerize upon irradiation under any set of conditions tried. This work needs to be continued to determine whether this is due to single molecule isolation or to other circumstances such as enhanced intersystem crossing. Note that CuCl cannot be used as a host for anthracene at 100°C since the dopant mobility is then such that it all escapes in a matter of a few hours.

(b) A high concentration of adamantyl azide (1:200 matrix ratio) is permanently incorporated in cesium iodide. It was photochemically converted into the highly reactive bridgehead imine, azahomoadamantene. In neat state this molecule dimerizes rapidly at 40K. In the cesium iodide environment it was stable to dimerization until about -100°C. Some of it survived nearly to room temperature, but complete dimerization was observed after a while at room temperature. This behavior was very similar to that observed for the same molecule incorporated into a polyethylene sheet, and suggests considerable internal mobility at room temperature. Yet, the organic material does not escape to the outside of the matrix. Work with this material needs to be

repeated at higher matrix dilution ratios. Because of the large size of the molecule it is possible that the lattice structure of the cesium iodide solid is completely disturbed when such a high matrix ratio is used.

(c) Several metal carbonyls have been incorporated into cesium iodide. Samples are perfectly stable at room temperature. The photochemical behavior was followed by ir spectroscopy. Upon low temperature irradiation, both octahedral carbonyls used, Mo(CO)_6 and W(CO)_6 , yield the corresponding pentacarbonyls and free CO. This behavior parallels that observed in argon matrices at very low temperatures. The pentacarbonyls are stable in cesium iodide but the back reaction in which the CO adds to the pentacarbonyl to yield the starting hexacarbonyl becomes observable at 100K. It is fast enough at room temperature to prevent observation of the pentacarbonyl in a sample which is not under irradiation. No dimerization or higher aggregation of these carbonyls has been observed in our experiments.

Most interesting behavior has been found for Fe(CO)_5 in CsI. This was studied at several matrix ratios ranging from 1:300 to 1:1600. This molecule is photoisomerized upon irradiation but no free CO is observed even when 95% of the starting pentacarbonyl is destroyed. The isomeric photoproduct is stable under further irradiation and shows no ESR signal. It is stable indefinitely at low temperatures. At room temperature it slowly rearranges back to the starting iron pentacarbonyl over a period of several days, giving complete recovery. This behavior is strikingly different from the behavior of iron pentacarbonyl in other matrices, such as argon, in which photodissociation to lower carbonyls and free CO occurs. It is a first demonstration of a striking environmental effect in our high temperature matrices compared with the usual inert matrices. The structure which is now under consideration for the isomeric compound on the basis of spectral evidence is tetragonal C_{4v} iron pentacarbonyl (tetragonal monopyramid). Further work is required to confirm this result which would represent the first observation of an isomer of iron pentacarbonyl.

Metal carbonyls are unstable thermally. Thus, it was of interest to investigate the thermal decomposition of our samples. The sample of iron pentacarbonyl incorporated in CsI decomposes above 150°C and leaves "metallic" iron in the matrix while more volatile components escape. Iron content in the resulting paramagnetic (ESR) matrix is 1:2000, essentially independent of the initial matrix isolation ratio for the carbonyl. What needs to be done next is to determine the state of aggregation of the iron in the cesium iodide matrix. Is it present as single atoms, small clusters, large clusters or metallic particles? If it is present as very small particles the material may have very interesting catalytic properties. It can also be dissolved in a solvent which has adequate dissolving power for CsI and the iron present may show unusual chemical reactivity towards various agents. Once again, more work needs to be performed in order to explore these possibilities and to extend the work to other metals.

In summary, a tentative answer to the second question is that conditions for single molecule isolation can probably be developed if additional effort is expended. There will almost certainly require a deposition temperature lower than 77K.

(iii) Finally, we have also made a few preliminary investigations of the use of co-deposited materials as actual sensors, even though the question of specific adsorption has not yet been settled satisfactorily. We have found to our delight that chemical specificity resulted from the doping even though it most likely was not due to specific adsorption in "footprints." The most encouraging results were obtained with a thin-layer overcoat of doped CuCl on top of a Te layer. Strong and fairly specific response in the conductivity of the layer was found for several vapors (chlorobenzene, hydrogen sulfide). These results also have obvious technological implications and it appears quite likely that useful detectors could be developed along these lines.

In conclusion, we believe that the new room-temperature matrix guest-host composites show considerable promise in a variety of applications, including specific sensor development, and warrant further investigation.

Publications:

- (1) One conference report given at the ACS Middle Atlantic Regional Meeting, 6-8 April 1983, Pocono Hershey Resort, White Haven, Pennsylvania.
- (2) One manuscript under preparation.
- (3) One patent application.

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